The Crystal Structure of Dichloro-(2,9-dimethyl-1,10-phenanthroline)zinc(II)

By H. S. PRESTON and C. H. L. KENNARD*
(*Department of Chemistry, University of Queensland, Brisbane, Australia*)

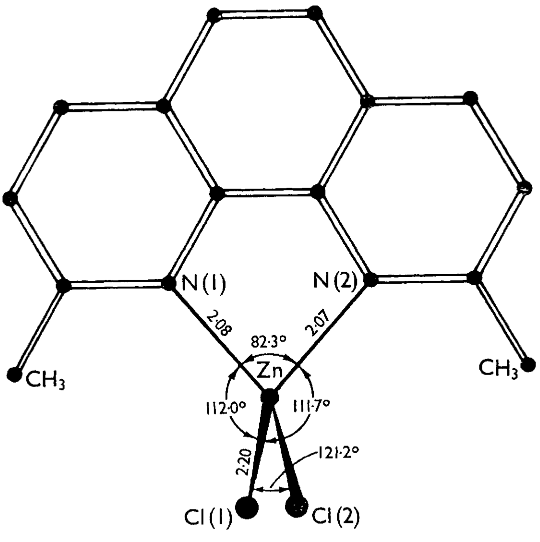
USING the ligand 2,9-dimethyl-1,10-phenanthroline (dmp) Fox, Hall, and Plowman[1] have prepared, and characterised a series of mono-complexes of the type $[M(dmp)X_2]$, where $M = Fe^{II}$, Co^{II}, Ni^{II}, and $X = Cl$, Br, I, SCN, NO_3, $\frac{1}{2}(SO_4)$. From magnetic susceptibility and visible-spectral studies, they predicted, in most cases, a distorted tetrahedral environment for the metal atom. Since tetrahedral co-ordination is common for the zinc atom, it was decided to prepare and determine the structure of $Zn(dmp)Cl_2$, and then follow this with structural work on the corresponding Fe, Co, and Ni complexes.

White $Zn(dmp)Cl_2$ was prepared by the addition of (dmp) in ethanol to an excess of $ZnCl_2$ in aqueous solution. These prismatic crystals, elongated along the *c*-axis, were grown from acetone.

Crystal data:—$C_{14}H_{12}Cl_2N_2Zn$; *M*, 344·5; orthorhombic; $a = 11{\cdot}21 \pm 0{\cdot}03$; $b = 17{\cdot}67 \pm 0{\cdot}03$; $c = 7{\cdot}48 \pm 0{\cdot}02$ Å; $U = 1482$ Å^{-3}, $D_m = 1{\cdot}56$ g.cm.$^{-1}$ (by flotation); $Z = 4$, $D_c = 1{\cdot}54$ g.cm.$^{-3}$; $F(000) = 696$. Space group *Pnam* (D_{2h}^{16}) or $Pna2_1$ (C_{2v}^{9}), Cu-K_α radiation, nickel filtered, single-crystal oscillation and Weissenberg photographs. 1116 nonzero reflections were recorded from seven levels (*hk*0 to *hk*6), on multiple-film Weissenberg photographs. Systematic absences indicated that the space group was either $Pna2_1$ or *Pnam*. An intensity distribution curve,[2] based on general reflections, indicated a centre of symmetry; consequently *Pnam* was chosen.

The co-ordinates of the zinc atom were obtained from a three-dimensional Patterson synthesis. The other atoms, except for hydrogens, were located in subsequent Fourier syntheses. Five cycles of full-matrix least-squares refinement using individual isotropic temperature factors gave an *R* value of 13·2%.

Each molecule occupies a special position in the cell, having all its atoms except the chlorines, in a crystallographic mirror plane, and the chlorines straddling the mirror plane. Apart from this crystallographically imposed (C_h) symmetry, the molecules approximate very closely to C_{2v} symmetry. The zinc atom has a distorted tetrahedral environment. The observed deviation from tetrahedral bond angles, (Figure), is undoubtedly due to the rigidity of the nitrogen atoms in the 2,9-dimethyl-1,10-phenanthroline ring system. The structure of dichloro-1,10-phenanthrolinezinc[3] shows a similar deviation with a N–Zn–N bond angle of 80·4°. In this case, however, the structure



FIGURE

is less symmetrical, having a variation in the N–Zn–Cl bond angles not observed in Zn(dmp)Cl_2. Nevertheless, bond lengths are very similar in both structures.

Preliminary powder and single crystal photographs have shown that Zn(dmp)Cl_2 is isostructural with Fe(dmp)Cl_2, Co(dmp)Cl_2, and Ni(dmp)Cl_2.[4]

We thank Dr. J. Taylor of the Australian Atomic Energy Commission for his interest and help during the computation.

(*Received, May 8th,* 1967; *Com.* 432.)

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